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during Oxidation Reactions[†]**

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EXAFS and Activity Studies of the Poisoning Effect of Cl on Pt/Al₂O₃ Catalysts during Oxidation Reactions

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ABSTRACT

The effect of Cl on the activity of Pt/Al₂O₃ catalysts for methane oxidation has been studied by H₂ and CO chemisorption, O₂ isotopic exchange, kinetic studies and EXAFS spectroscopy. Catalysts containing 1.5% Pt/Al₂O₃ were prepared by incipient wetness from H₂PtCl₆ and Pt(NH₃)₄(NO₃)₂ precursors. Both reduced catalysts have similar dispersion (0.8) as determined by H₂ chemisorption. At low methane concentration (0.3 vol.% CH₄, 16 vol.% O₂) the Cl-free catalyst was about 20 times more active during complete methane oxidation than the Cl-containing catalyst. Both CO chemisorption and oxygen exchange were observed on the Cl-free catalyst, whereas they were not detected on the Cl-containing catalyst. On the Cl-free catalyst, only Pt-Pt and Pt-O bonds were detected from the EXAFS results, while on the Cl-containing catalyst additional Pt-Cl bonds were present.

The effect of chlorine on activity strongly depended on the reactant concentration. Exposure of the Cl-free catalyst to higher concentrations of methane (3 vol.% CH₄) reduced the activity to a level similar to that of the Cl-containing catalyst. Addition of HCl to the Cl-free catalyst rendered the activity identical to the catalyst prepared from Cl-containing precursors. A model is proposed to explain the mechanism of chloride poisoning, which appears to be site blocking.

INTRODUCTION

The complete combustion of methane by Pt and Pd catalysts has been studied in relation to pollution control of emissions from natural gas vehicles (NGV) [1], as well as for the oxidation of methane in turbines for power generation [2]. Supported Pt catalysts are often prepared from Cl-containing precursors such as H₂PtCl₆, and it has been reported [3-5] that Cl poisons the oxidation activity. The state of the active catalyst's surface and the effect of Cl poisoning on the activity, however, have not been elucidated.

Liebske et al. [6] were among the first to propose a model of the various phases that could be present as a function of pretreatment conditions in a Pt/Al₂O₃ catalyst prepared from Cl precursors. These phases, however, were not correlated with the catalyst's activity. Based on temperature-programmed reduction (TPR) of Pt catalysts oxidized at different temperatures, Hwang and Yeh [7] concluded that four types of oxide species could be formed. These authors proposed that at room temperature there is a surface oxide, PtO_{0.7}. At 100°C PtO is formed, while at 300°C Pt further oxidized to PtO₂. Oxidation at 600°C leads to metallic Pt and platinum aluminate. In addition, preparation of the catalyst from a PtCl₄ precursor results in a PtO_xCl_y complex, which can be removed by reduction in H₂ at 400°C [3]. In a similar study, Burch and Loader [8] concluded that the oxidation activity of Pt catalysts was optimal for a partially oxidized and reduced surface.

Farrauto et al. [3] reported that the presence of Cl on the catalyst reduced the methane oxidation activity of Pd/Al₂O₃, and that removal of Cl increased the catalyst's activity. Similarly, Marceau et al. [4] found that elimination of Cl from Pt/Al₂O₃ catalysts at 450°C led to higher activity. Roth et al. [5] also confirmed that removal of Cl from a Pd(Cl)/Al₂O₃ catalyst led to the same activity as Cl-free Pd catalysts and suggested that the active sites are PdO that slowly deactivates to form a less active Pd(OH)₂.

The objective of this work is to determine the structure of the active Pt species for methane oxidation and to characterize the state of the surface on Cl-free and Cl-containing Pt/alumina catalysts. EXAFS spectroscopy probes the local structure around a selected element – important for a study of highly dispersed catalysts for which long range order does not exist and x-ray diffraction may not be an appropriate technique.

EXPERIMENTAL.

Catalyst Preparation

1.5% Pt/Alumina (Cl): To 11.7 g of Catapal alumina calcined at 500°C (SA = 203 m²/g, pore vol. = 0.42 cc/g) was added 0.467 g of H₂PtCl₆ (37.5% Pt) in 9 ml H₂O. The catalyst was dried and calcined at 500°C for 2 h. Elemental analysis indicated 2.1% Cl, and the hydrogen chemisorption (T = 25°C) of the reduced catalyst was 0.71 cc/g, or a dispersion of 0.82.

1.5% Pt/Alumina (Cl-free): To 15.0 g of Catapal alumina was added 0.60 g of Pt(NH₃)₄(NO₃)₂ in 11 ml H₂O. The catalyst was dried overnight and calcined at 250° for 2 h. The hydrogen chemisorption of the reduced catalyst (T = 25°C) was 0.70 cc/g, or a dispersion of 0.81.

The catalysts were reduced in flowing H₂ (200 cc/min) at 300°C for 2 hr. The pre-reduced catalysts were oxidized prior to measurements related to CH₄ oxidation, isotopic O₂ exchange, CO chemisorption, and EXAFS spectroscopy.

CO Chemisorption of the Oxidized Catalyst

The pre-reduced Pt catalysts were heated to 350°C (at 10°C/min) in flowing air and maintained at that temperature for 45 min. The samples were cooled to room temperature in He and dosed with CO in He until the concentration at the outlet was identical to the inlet. The 1.5% Pt/alumina with Cl did not adsorb CO, while the 1.5% Pt/alumina without Cl adsorbed 0.2594 cc/g of CO. Assuming that CO/Pt is 1.0 at room temperature, 15% of the Pt atoms were exposed in the latter (oxidized) catalyst.

Isotopic Oxygen Exchange

100 mg of catalyst was heated in air to 350°C at 10°C/min and maintained at that temperature for 30 min. In flowing He, the temperature was decreased to 30°C, and the feed was switched to 4.0% ¹⁶O₂-4.0% ¹⁸O₂ (balance He) at a flow rate of 40 cc/min. The isotopic reaction products were detected by a Fison's Gaslab 300 quadrupole mass spectrometer. The isotopic composition of the reactants was determined without added catalyst.

Catalytic Activity

Catalyst activities were determined in a quartz reactor (12 in. long, ½-in. dia) equipped with an external recycle pump. The effluent flow rate was 130 cc/min, and the recycle ratio was about 20 to ensure complete mixing. Only small differences in activity were obtained for (prereduced) catalysts treated in O₂ or H₂ followed by O₂. Hence, prior to each run the catalyst was pretreated in air at 300°C for 2 h. The catalyst was cooled to room temperature, and switched

to the reaction mixture, and the temperature was increased to about 450°C. (Hydrogen chemisorption of metallic Pt particles oxidized up to 500°C showed no significant change in dispersion.) Catalyst activities were obtained with dilute methane concentrations: 0.3% CH₄, 16% O₂, balance He or 3.0% CH₄, 16% O₂, and balance He. The methane conversions were reproducible within 5%. Reaction rates were calculated at various temperatures directly from the conversion assuming complete mixing due to the large recycle ratio used. Turnover frequencies were calculated from dispersion values obtained for the freshly reduced surface and plotted vs. 1/T to obtain activation energies.

EXAFS Data Collection and Analysis

Measurements using extended x-ray absorption fine-structure (EXAFS) spectroscopy were made on the insertion-device beam line of the Materials Research Collaborative Access Team (MRCAT) at the Advanced Photon Source, Argonne National Laboratory. Measurements were made in transmission mode with ionization chambers optimized for the maximum current with linear response ($\sim 10^{10}$ photons detected/sec). A cryogenically cooled double-crystal Si (111) monochromator with resolution (ΔE) better than 2.5 eV at 11.564 keV (Pt L₃ edge) was used in conjunction with a Rh-coated mirror to minimize the presence of harmonics [9]. The integration time per data point was 1-3 sec, and three scans were obtained for each processing condition.

The sample thickness was chosen to give an absorbance ($\Delta\mu x$) of about 1.0 in the Pt edge region, corresponding to approximately 100 mg of catalyst. The sample was centered in a continuous-flow *in-situ* EXAFS reactor tube (18 in. long, 0.75-in. dia) fitted at both ends with polyimide windows. The calcined catalysts were first measured in air at room temperature. The catalysts were then reduced in 5% H₂ (balance He) at 300°C for 1 h and cooled to room temperature. The second series of EXAFS data were collected at room temperature in H₂. Thereafter, the pre-reduced catalysts were purged with He at room temperature, then heated to 300°C in 5% O₂ (balance He) for 1 h. After the oxidizing pretreatment, the EXAFS data were collected at room temperature in O₂.

Standard procedures based on WINXAS97 software [10] were used to extract the EXAFS data. Phase shifts and backscattering amplitudes were obtained from EXAFS data for reference compounds: Na₂Pt(OH)₆ for Pt-O, H₂PtCl₆ for Pt-Cl, and Pt foil for Pt-Pt.

RESULTS AND DISCUSSION

Catalytic Activity

Figure 1a shows the effect of Cl on methane conversion at different temperatures for the 1.5% Pt/alumina catalysts prepared from Pt(NH₃)₄(NO₃)₂ (Cl-free) and H₂PtCl₆ (with Cl). Although both catalysts have nearly identical Pt loading and particle size, the catalyst prepared from H₂PtCl₆ (2.0 wt.% Cl) requires about 150°C higher temperature to obtain the same methane conversion. This corresponds to a 20-fold change in reaction rate (units of moles CO₂ produced per second per mole Pt exposed) at 350°C. Calculations from the two Arrhenius plots shown in Figure 1b indicate that the two catalysts have similar activation energies, 107.47 and 90.93 kJ/mol for the Cl-containing and Cl-free catalyst, respectively. At the higher methane concentration tested (not shown in figure), a similar effect of Cl on the oxidation activity is observed; however, the difference in activity of the two catalysts is not as large as for the lower methane concentration. With 3% CH₄, the Cl containing catalyst requires a temperature approximately 50°C higher to obtain the same conversion, which corresponds to a reaction rate about 7 times lower at 400°C. In addition, the activation energies increase significantly for both catalysts, 147.13 kJ/mol for the Cl-free and 161.67 kJ/mol for the Cl-containing catalyst.

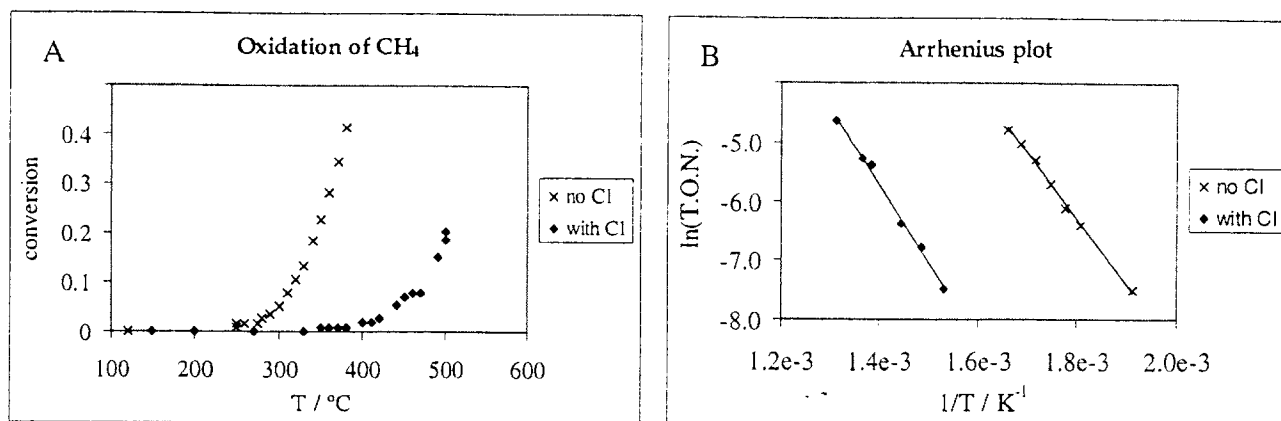


Fig. 1. Methane conversion vs. temperature for Pt/alumina catalysts with and without Cl. Feed composition: 0.3% CH₄, 16% O₂, balance He.

To further demonstrate the effect of Cl on the oxidation activity, HCl was added at room temperature to the Cl-free catalyst to give a Cl content of about 2 wt.%, which is similar to the Cl present on the catalyst prepared from chloroplatinic acid. Conversion as a function of temperature for these catalysts is shown in Fig. 2. Addition of HCl to the Cl-free Pt/alumina catalyst renders its activity nearly identical to that of the Cl-containing catalyst. Calcination after HCl addition had little effect on the catalyst activity since, in the case of methane, the reaction starts at a temperature higher than the calcination temperature of 300°C. Addition of Cl in excess (5 wt.% Cl) had no additional effect on the activity, perhaps indicating saturation of the Cl coverage of the Pt surface.

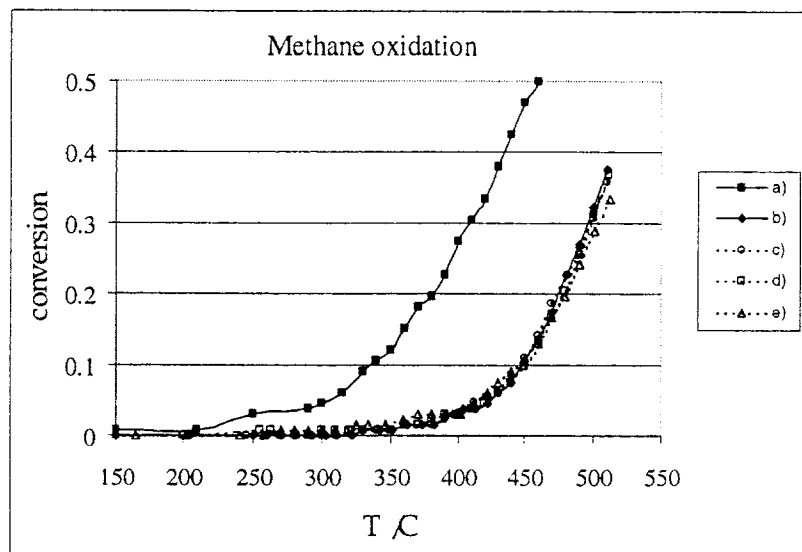


Fig. 2. Methane conversion vs. temperature for Pt/alumina catalysts prepared by different methods. Feed composition: 0.3% CH₄, 16% O₂, balance He.

- a) No Cl,
- b) Cl containing,
- c) addition of 2% Cl⁻ and calcination at 300°C,
- d) addition of Cl⁻ in excess and calcination at 300°C, and
- e) addition of 2% Cl⁻, no calcinations.

In parallel studies of the effect of Cl on CO oxidation over Pt/Al₂O₃ catalysts, when the activity was measured immediately after addition of HCl without calcination pretreatment, the activity was similar to the Cl-free catalyst (light-off temperature for CO oxidation is about 125°C). However, after calcination at 300°C, the activity decreased significantly, and it was comparable to the catalyst prepared from chloroplatinic acid. This suggests that at first the HCl is

adsorbed mainly by the Al_2O_3 support, and during calcination it desorbs from the support and is adsorbed on the surface of Pt, decreasing the catalyst activity. This effect is not seen during methane oxidation because the reaction temperature for the Cl-free catalyst is higher than the calcination temperature. Therefore, as the catalyst is heated, the Cl, originally on the support, would migrate to the metal particles before the reaction takes place, having a similar effect to calcination.

In an early paper, Newkirk and McKee [11] suggested that in $\text{Rh}/\text{Al}_2\text{O}_3$, $\text{Ru}/\text{Al}_2\text{O}_3$, and $\text{Ir}/\text{Al}_2\text{O}_3$ catalysts prepared from Cl-containing precursors, Cl is adsorbed by the support when decomposition of the precursor takes place. This observation agrees with our results. Those authors also found that reduction of metal particles by H_2 in these catalysts occurs readily at low temperatures (150°C - 200°C) due to reaction with H_2 to form HCl . In an oxygen environment, however, decomposition of the halide and formation of PtO species require much higher temperatures.

EXAFS Analysis

The EXAFS data were collected for the calcined, reduced, and oxidized Pt catalysts. The results of the multiple-shell model fits are given in Table 1. Calcination of Pt catalysts leads to Pt(IV) with 6 nearest neighbors: 6 Pt-O in the Cl-free catalyst, and 2.5 Cl and 3.5 O in the Pt/alumina with Cl. No Pt-Pt bonds are observed in the calcined catalysts. The Pt-O coordination distance of about 2.06 \AA is characteristic of a Pt(IV) -oxide bond, and the Pt-Cl distance of 2.31 \AA is (within experimental error) identical to that in chloroplatinic acid [12]. Reaction at 300°C in H_2 results in the complete reduction to small metallic Pt particles. A fully coordinated shell in Pt metal consists of 12 nearest-neighbor Pt atoms. The coordination numbers of 6.6 and 6.9 Pt neighbors for the two catalysts in Table 1 show that, on average, the first shell of every Pt atom is not completely coordinated to Pt, indicating small metallic Pt cores. Assuming a compact geometry and that the Debye-Waller factor, σ^2 , has been modeled correctly, the average particle diameter is $9 \pm 3 \text{ \AA}$. These values are consistent with the H_2 chemisorption results, indicating that the dispersions are 0.8.

The signal of reduced Pt particles is sufficiently small that there is a contribution to the EXAFS from the oxygen ions of the support. The Pt-O distance of $2.20 \pm 0.01 \text{ \AA}$ is similar to that previously reported for Pt, Rh, and Ir catalysts [13]. The Pt-Pt distance of 2.7 \AA and the coordination numbers of 3.6 (Cl-free) and 0.9 (Cl) indicate that the small metallic Pt particles are not fully oxidized at 300°C by oxygen. The Cl-free catalyst has 3.9 Pt-O bonds, while the Cl-containing catalyst has 2.0 Pt-O and 2.5 Pt-Cl bonds. Identical results were obtained for the oxidized catalysts treated with O_2 alone, 0.3% CH_4 and 16% O_2 , or 3% CH_4 and 16% O_2 at 300 and 450°C . Finally, after oxidation, both catalysts were re-reduced in H_2 at 300°C , and again the results were identical to those obtained prior to oxidation. This finding indicates no sintering of the Pt during oxidation.

Figure 3 shows the k^3 -weighted Fourier transform of the EXAFS and the model fit for the oxidized Cl-free and Cl-containing Pt catalysts. Even though the magnitude of the transform is similar, the imaginary component is significantly different, a result of the addition of Cl neighbors in panel B.

Table 1. Results from EXAFS Fits (k^3 , $\Delta k=3.1-12.5$, $\Delta r=1.3-3.0$)					
Treatment	Scattering Path	Coord. Num.	R, Å	$\Delta\sigma^2$, Å ² ($\times 10^{-3}$)	ΔE_0 , eV
1.5% Pt/alumina (Cl-free)					
Calcined at 250°C	Pt-O	5.9	2.06	0.50	1.76
Reduced at 300°C	Pt-O	1.1	2.19	10.6	17.5
	Pt-Pt	6.6	2.74	2.36	-2.98
Oxidized at 300°C, 5% O₂	Pt-O	3.9	2.04	4.46	0.75
	Pt-Pt	3.6	2.70	8.26	-0.90
1.5% Pt/alumina (Cl)					
Calcined at 300°C	Pt-O	3.5	2.03	-1.36	-.024
	Pt-Cl	2.5	2.31	-1.36	-1.21
Reduced at 300°C	Pt-O	0.9	2.21	2.22	17.4
	Pt-Pt	6.9	2.74	2.36	-2.92
Oxidized at 300°C, 5% O₂	Pt-O	2.0	2.05	4.63	1.63
	Pt-Cl	2.5	2.31	4.63	5.19
	Pt-Pt	0.9	2.70	1.54	-0.46

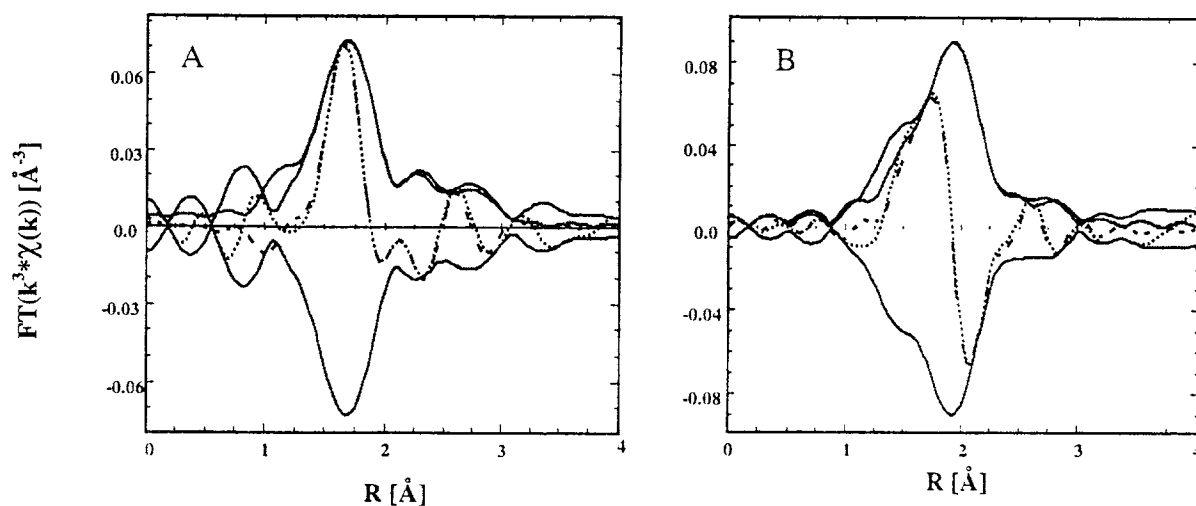


Fig. 3. Fourier transform of Pt EXAFS. Solid lines: magnitude (red, raw data; blue, model fit). Dotted line: imaginary part (red, raw data; black, model fit). (A) 1.5% Pt/alumina without Cl and (B) 1.5% Pt/alumina with 2.0% Cl.

Additional Characterizations

The oxidized (prereduced) catalyst was also characterized by CO chemisorption. While there was no CO chemisorption on the Pt/alumina with Cl, about 15% of the Pt atoms adsorbed CO in the Cl-free catalyst. Since CO readily chemisorbs on metallic Pt but not on oxidized Pt, these results suggest that the surface of the Pt/alumina with Cl is fully oxidized, i.e., fully covered by Pt-Cl and Pt-O bonds. In the Pt/alumina without Cl, however, there are both oxidized Pt and exposed metallic Pt atoms.

Since reduced Pt dissociatively chemisorbs O_2 at room temperature, the catalysts were evaluated for isotopic exchange of a 50:50 mixture of $^{16}O_2$ - $^{18}O_2$. Assuming that 15% of the Pt atoms in the oxidized Pt/alumina without Cl are active, the turnover rate (TOR) was 0.36 sec^{-1} , while for the Pt/alumina with Cl there was no isotopic exchange. Both the CO chemisorption and isotopic exchange of O_2 indicate that exposed metallic Pt atoms are present in the Pt/alumina without Cl oxidized at 300°C . In addition, the Pt/alumina with Cl has no exposed metallic Pt atoms.

Model of Cl Poisoning

A model depicting the Pt species after the various treatments is shown in Figure 4.

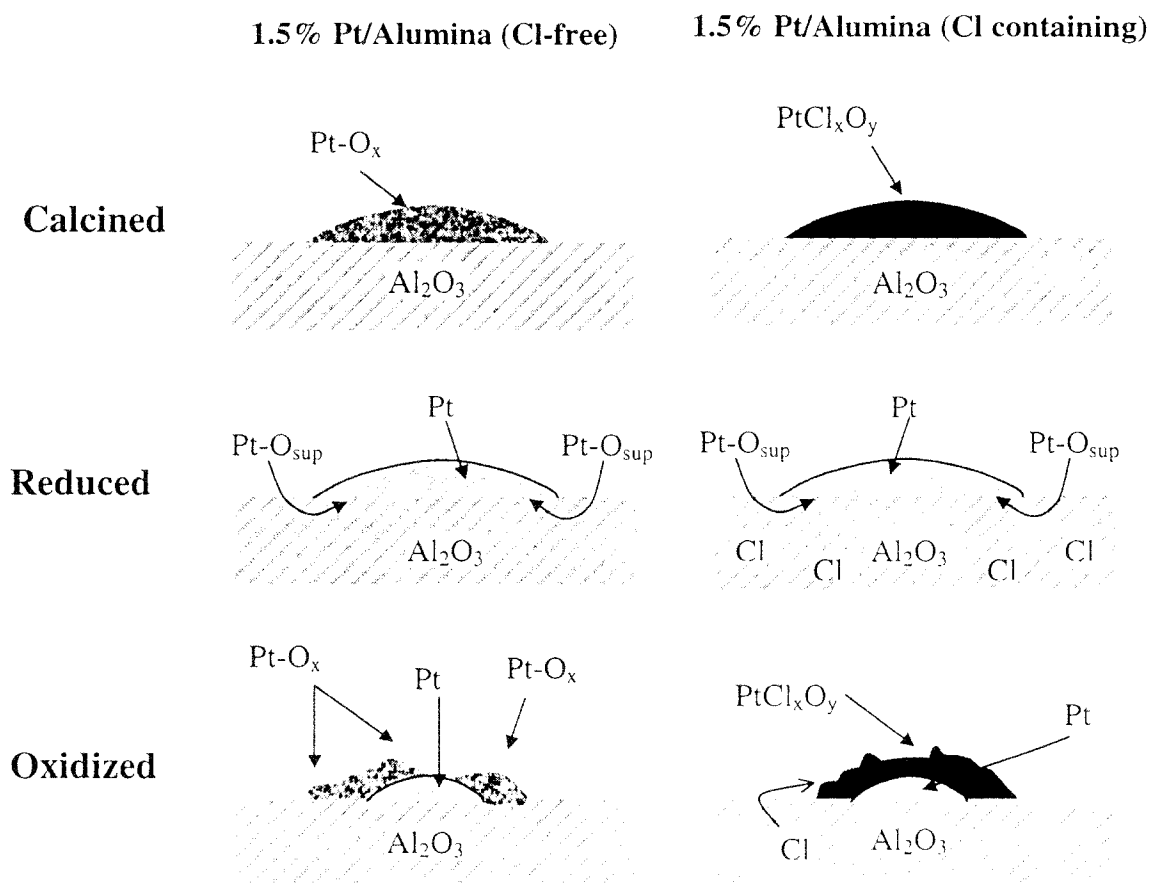


Fig. 4. Model depicting the Pt species after the various treatments.

Upon calcination, the Pt is present as a platinum(IV) oxide phase (Cl-free) or a platinum(IV) oxychloride phase (with Cl). Since there are no apparent Pt-Pt bonds, the oxide is present as very small particles or is highly disordered. Reduction of the calcined catalysts leads to small metallic particles in contact with the oxygen ions from the alumina support. In the Cl catalyst, there are no longer any Pt-Cl bonds. Oxidation at 300°C leads to oxidation of the surface, but the Pt particles are not fully oxidized. The Cl-free catalyst still has exposed, reduced Pt atoms at the particle surface, which chemisorb CO, undergo oxygen isotopic exchange, and are active for methane oxidation. These results also suggest that the active site is metallic Pt. This model agrees well with that proposed by Burch and Loader [8] who concluded that neither a fully reduced nor a fully oxidized surface is optimal for methane oxidation. While oxidized Pt/alumina with Cl also has a metallic core – possibly as small as two Pt atoms – the surface contains both Pt-O and Pt-Cl bonds. Since no Pt-Cl bonds occur in the reduced catalyst, it is likely that the Cl bound to the alumina support migrates to the Pt surface during oxidation. The inability of this catalyst to adsorb CO or induce O₂ isotopic exchange suggests that no reduced Pt atoms appear on the surface. The low methane oxidation activity is likely due to the nearly complete coverage of the surface by Cl (and O). The mechanism of chloride poisoning, therefore, appears to be site blocking.

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